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by

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ABSTRACT

A hematite precipitate containing 450 ppm silver that had been produced in an experimental zinc circuit was leached with thiourea solutions. The effects of thiourea concentration, pulp density and leaching time on the percentage extraction of silver and the extent of thiourea decomposition in a 1% H_2SO_4 medium were studied. Under the most advantageous conditions, the silver could be extracted with an approximate economic advantage of $49 per metric ton of precipitate. It was found that under conditions of high thiourea decomposition and long leach times, impurity buildup may be a factor in the viability of the process.

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LESSIVAGE A LA THIOUREE DE L'ARGENT CONTENU DANS UN PRECIPITE D'HEMATITE

par

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RESUME

Un précipité d'hématite contenant 450 ppm d'argent produit dans un circuit de zinc expérimental a été lessivé avec des solutions de thiourée. Les effets de la concentration de thiourée, de la densité de la pâte et du temps de lessivage sur le pourcentage d'argent extrait et l'ampleur de la décomposition de la thiourée dans un milieu titrant 1 % de H_2SO_4 ont été étudiés. Dans les conditions les plus optimales, la rentabilité de l'extraction de l'argent se chiffrerait à environ 49 $ par tonne métrique de précipité. On a découvert que, dans des conditions de forte décomposition de la thiourée et de longs temps de lessivage, l'accumulation d'impuretés peut être déterminante pour la viabilité du procédé.

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INTRODUCTION

Thiourea leaching is an alternate technology to brine leaching or cyanidation for silver recovery from process residues (1). Important variables in determining the viability of thiourea leaching are the extent and value of silver extraction and the decomposition of the thiourea. Some very fine grained residues are not amenable to thorough mineralogical investigation and thus the silver containing phases as well as other compounds which may consume thiourea and contribute to the inefficiency of the process remain ill-defined. In most cases of silver leaching from residues, it is difficult to predict leaching behaviour and it is necessary to examine each case experimentally to determine the stoichiometry and economics of operation.

Previous work with gold-thiourea leach systems has revealed that the optimum conditions for leaching are relatively low temperatures ($<40^{o}C$), low thiourea concentrations ($\leq$2-10% thiourea) and acidic conditions (1%-5% H_2SO_4) (1). A particularly troublesome aqueous species is ferric ion which, when present in appreciable concentrations, causes excessive thiourea decomposition.

A study of the leaching of a hematite precipitate from an experimental zinc processing circuit is outlined in this report. The silver content of the hematite precipitate was approximately 450 ppm. Because of the very fine particle sizes involved (<5 μm), the silver phases could not be well defined but likely consist of silver chloride, silver sulphide, silver jarosite and silver sulphate. Most of the iron in the precipitate is not leachable (2) and thus should not cause excessive decomposition of the thiourea. A number of tests were performed on the limited quantity of available precipitate at room temperature with 1.5 to 33% solids, thiourea concentrations of 2% and 10% and an acid level of 1% H_2SO_4. Leached (aqueous) silver, thiourea concentrations before and after leaching, initial and final pH and silver

content remaining in the leached residue (where possible) were determined. A figure of merit calculation was used to rank the viability of the leaching conditions.

METHOD

The hematite precipitate was formed in an experimental zinc processing circuit. Chemical analyses done at CANMET indicate that the sample contains 456 ppm Ag.

Reagent grade chemicals and distilled water were used to make the solutions. In a typical experiment, the desired amount of precipitate (3.0 gm for 1.5%, 30 gm for 13% and 100 gm for 33% solids) was combined with 200 mL of the acidic thiourea solution in a 600 mL beaker, and was stirred magnetically for the prescribed time. The slurry was then filtered once through a Buchner funnel and subsequently through a Millipore 0.45 μm filter. This second filtration was needed because the fine particles of the residue passed through the Buchner filter. Soluble silver was measured by atomic absorption spectroscopy and thiourea was determined by mercuric nitrate titration with diphenylcarbazide as the indicator (3). Silver retained in the solid was analysed by fire assaying with an atomic absorption finish.

The rationale for leaching silver with thiourea can be equated to the difference in the value obtained from the silver dissolved from the solid and the value lost by resultant thiourea decomposition. The analyses for silver and the mercuric nitrate titration gave estimates for silver recovery from the solid and the extent of thiourea decomposition, respectively. The two parameters, silver recovery and thiourea losses were computed and normalized to a metric ton (1000 kg) of precipitate to yield a figure of

merit based on the value of silver recovered less the value of thiourea decomposed. This calculation does not reflect any costs of processing or silver recovery from the leach solution.

RESULTS AND DISCUSSION

Table 1 summarizes the leach conditions and analytical results for the tests performed (#101-106). The extent of testing was constrained by the limited amount of precipitate available.

(a) 1.5% Solids (2% tu - 1% H_2SO_4)

The leach times investigated were 1 (#101), 18 (#102) and 24 (#103) hours. The final silver contents of the solids were 315, 322 and 260 ppm, respectively; up to 72% Ag extraction was obtained. The 24 h test was not really diagnostic because the stirring stopped sometime during the test. The corresponding thiourea consumptions were 36, 169 and 132 kg/t (kilograms of thiourea per metric ton precipitate). The consumption may be high because the relatively small amount of hematite precipitate increases the uncertainty in the calculation. In the 24 hour test, the final pH was also measured. It was found to be 1.2 and this represents a modest change from the initial value of 0.7; acid consumption was not significant in any of the tests.

Silver extractions did not increase greatly after 1 h as evidenced by the silver content of residues from the 1 hour (#101) test compared to the 18 hour test (#102), 145 and 134 ppm, respectively. The decomposition of thiourea, however, was much greater in the 18 hour test (169 kg/mt) compared to the 1 hour test (36 kg/mt). A white precipitate was found in the filtrates from the #102 and #103 tests after standing one day. The soluble silver concentrations were the same after the precipitation of the white solid. After

nitric acid digestion of the white precipitate, subsequent testing with chloride ion additions did not reveal any AgCl turbidity. No silver was contained in this precipitate or similar ones produced in all later tests. After drying and consolidation, the precipitate had a yellowish tinge and looked very similar to elemental sulphur. The white precipitate may have consisted of, at least partially, finely divided elemental sulphur. A larger scale leach would be required to yield a sample size suitable for a more exact compositional analysis.

The figure of merit calculation representing the difference between the value of silver extracted and the cost of thiourea decomposed can be calculated as described in the Methods section. It is assumed that the price of silver is \$10/oz (35.2 oz/kg) and that of thiourea is \$2/kg. For #101, #102 and #103, the differentials were \$38, -\$226 and -\$173; clearly thiourea decomposition made the last two leach conditions uneconomical although it was also seen that leaching for more than one hour was unnecessary at these low percentage solids.

The final concentration of dissolved silver of 3 to 4 mgL^{-1} (single pass) is too low for economic recovery. Higher percent solids would be needed to increase the silver concentration of the solution in a single stage leach.

(b) 13% Solids (2% tu - 1% H_2SO_4)

Two tests were performed at 13% solids and using leaching time of 3 hours (#106) or 24 hours (#104). Comparing #104 with #103 (1.5% solids, 24 h), it is seen that the final silver concentration (45 mgL^{-1} vs 3 mgL^{-1}) is higher and that the thiourea decomposition (22 kg/mt vs 132 kg/mt) is lower for the higher pulp density test.

At 13% solids, higher silver extractions and higher thiourea decompositions were obtained when longer leaching times were employed. The figure of merit

differential between the silver value and thiourea cost at 24 and 6 hours are $49 (#104) and $48 (#106), respectively, and this indicates that these leaching conditions are potentially favourable.

The ideal situation would be the 60% silver extraction of #104 and the low thiourea consumption of 4 kg/mt of #105 and #106. It may be possible to achieve a compromise leach time between 6 and 24 hours at 13% solids which gives a maximum figure of merit.

The leach solutions from #104 and #106 were yellow in colour with #104 being more intensely yellow. This yellow colour is not completely removed on passage through the Millipore filter. The addition of H_3PO_4 does not fade the colour suggesting that Fe^{3+} is not responsible. The addition of HCl does cause the colour to disappear suggesting that the colour may be due to colloidal elemental sulphur or arsenic sulphide (As_2S_3); similar colours are seen when H_2S is bubbled through Fe^{3+} solution (S^o) or arsenic(III) solution (As_2S_3). Some elemental sulphur was separated on the Millipore filter in #104. Since the solution showing the highest thiourea decomposition (#104) had the most intense colour, the sulphur most likely came from the thiourea. It is conceivable that the filtrate from a leach similar to #104 would present handling problems due to sulphur buildup. Not only does a high thiourea decomposition affect the intrinsic economics of the process, but it might also increase the cost of leaching because of extra solution handling.

The white solid alluded to in the 1.5% solids results was also encountered during the 13% solids experiments.

(c) <u>33% Solids (2% tu - 1% H_2SO_4)</u>

One test (#105) was done with a high solids content and for 3 hours stirring. The slurry was difficult to handle due to the high viscosity and poor settling properties of the solids. The test results show that the

percentage Ag extraction and thiourea decomposition are similar to those realized at 13% solids (#106); the figure of merit is identical to the 13% solids leaches at $48. The silver in solution is fairly high (59 mgL^{-1}) and the pH change was minimal.

Solution analyses for iron, calcium, silicon and zinc were performed on the #106 filtrate. The iron concentration was 0.210 g/L and this represents approximately 0.2% of the iron originally in the sample. This soluble iron was all in the ferric state. Minimum amounts of silicon and calcium (0.002 and 0.007 gL^{-1}, respectively) were found. The zinc in solution was 0.130 gL^{-1} indicating that approximately 1000 ppm less zinc is contained in the solid after leaching. The iron and zinc concentrations are fairly high and should be closely followed in subsequent leaching work.

(d) 13% Solids (10% tu - 1% H_2SO_4)

An experiment with a nominal 10% tu concentration was performed in a manner similar to that of #106 using a 3 hour leach. The initial thiourea concentration was 98 gL^{-1} and this was reduced to 68 gL^{-1} at the completion of the leach. The final soluble silver concentration was 20 mgL^{-1}, indicating the dissolution of 170 ppm silver from the solid (36% of available silver). The consumption of thiourea was 79 kg/mt. The calculated figure of merit is -$98 and this indicates unfavourable conditions. The use of a higher concentration of thiourea resulted in a large increase in thiourea consumption but only a minimal increase in silver extraction.

Solution analyses for ferric ion, calcium, silicon and zinc gave 0.35, 0.022, 0.002 and 0.12 gL^{-1}, respectively. The iron dissolved was approximately 0.4% of that available. The silicon and calcium concentrations were minimal. The zinc concentration was similar to that observed in #106.

(e) Silver Balances

The balance between the silver content originally present in the precipitate and the silver contained in the leach residue and aqueous phase is an important consideration. The easiest method of verifying the silver balance is to examine the correlation between the calculated silver content of the leached hematite and the assayed value.

For the 1.5% solids tests, a 100% silver balance was assumed. The small amount of hematite used (<1 g) made it impossible for an accurate assay to be done.

For the 13% solids experiments, it was possible to compare the calculated silver contents to the assay values. The calculated silver values in #104, #105 and #106 were 120, 310 and 298 ppm, respectively. The corresponding assay values were 185, 290 and 298. The last two values agree well with the calculated assays although there is a discrepancy in the first test. Because of the limited data available, it is difficult to ascertain whether the discrepancy is due to analytical errors or to systematic errors in the process modelling. As an example of the latter, the homogeneity of the sample may not be perfect and the starting silver content may be different than that assumed.

(f) Immediate Concerns

It would be advantageous to collect more data on the effect of leaching time on the figure of merit at 13% solids as discussed in (b). Another factor is the effect of thiourea concentration. Higher levels of thiourea (10% in (d)) have been shown to be deleterious, but are lower levels more advantageous?

Additional samples of hematite precipitates should be obtained and the results of this work confirmed using this new material. A particularly important consideration is the silver balance. Efforts to obtain some correlation with silver content and silver speciation should be made.

(g) Future Concerns

Silver could be recovered from single-pass leaches as performed here, or from an aqueous solution which has experienced many 13% solids multistage leaches to increase the soluble silver concentrations. An interesting aspect of multistage leaching is the decreased thiourea decomposition at lower thiourea concentrations that may make this method economically viable. Methods of silver removal (IX, SX, electrolysis, cementation) will also have to be examined.

Acid prewashing of the feed solids has been found by some workers (1) to reduce the extent of thiourea decomposition. The use of this technique should be investigated for hematite precipitates as well.

Recent work on thiourea leaching has used SO_2 bubbling into the medium (4) to control the thiourea decomposition, and very good results have been obtained. This may be worth investigation here, also. Other methods such as addition of ferrous ion to moderate the oxidization potential of the ferric ion should be tested.

The buildup of impurities from thiourea decomposition and from the leaching of other minerals is also a concern. In the leach solutions, a yellow colour ascribed to sulphur or sulphur compounds was observed. A white precipitate was observed after the filtered leach solution stood for a day. The main decomposition products from thiourea are sulphur and most probably cyanamide (H_2NCN) (4), a common fertilizer. The analysis of some leach

solutions has revealed the leaching of some iron and zinc from the precipitate as well. A better understanding of sulphur disposition, impurity buildup and byproduct metal lixiviation is needed.

The work described here is essentially a non-oxidative leach. Silver minerals such as silver chloride or silver sulphide are known to react with thiourea in the absence of oxidizing agents. Any oxidant present came from the air (O_2) or was leached from the solid (Fe^{3+}). The effect of deliberately added oxidant (e.g., Fe^{3+}) on the figure of merit may give some insight into the viability of adding oxidants to increase either the silver extraction rates or the extent of Ag recovery (i.e., from other mineralization).

Although thioureation is an alternate method to brine leaching and cyanidation for silver recovery, a comparison among these methods is not possible because data on the brine leaching and cyanidation of the hematite precipitate are not available. It would be interesting to obtain comparative results with brine- and cyanide-based systems.

CONCLUSIONS

The limited thiourea leaching program reported above has shown that, under optimum conditions, high extractions of silver can be obtained from the ill-defined silver phases contained in a hematite precipitate made in an experimental zinc circuit. The preferred leaching conditions were 2% thiourea, 1% H_2SO_4, 24 hour residence time at room temperature and 13% solids, and these yielded a final silver concentration of 45 mgL^{-1}. Fifty-nine percent silver extraction occurred under these conditions. Higher thiourea concentrations and higher % solids had a detrimental effect on thiourea stability. Shorter leach times gave lower thiourea losses but also gave poorer silver extractions. The same overall economic advantage to the preferred leach conditions is

obtained at 13% solids, 2% thiourea, 1% H_2SO_4 at room temperature with a 3 hour leach. Similar economics were realized when the leaching was done at 33% solids. In these two cases, 35% Ag extraction was observed.

A yellow colour was seen in the filtered leach solution and a white precipitate formed upon standing suggesting that co-leached materials or decomposition products may be a factor in process viability. The acid consumption in all of the leach tests was not significant. Further work with a better characterized sample is needed.

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Table 1 - Leaching tests using 2% tu - 1% H_2SO_4 media

Test #	% Solids	Leach Time (h)	Final Thiourea (gL^{-1}) (a)	Thiourea Consumption g	Thiourea Consumption kg/t (b)	Final Soluble Ag (mgL^{-1})	Silver Remaining in Residue (ppm)	Figure of Merit (i)	% Extraction of Silver	Comment
101	1.5	1	18.2	0.46	36	4.2	145 (c)	38	68	
102	1.5	18	18.5	0.40	169	4.6	134 (c)	-226	71	(f)(h)
103	1.5	24	16.5	0.33	132	3.0	196 (c)	-173	6	(e)(f)
104	13	24	15.7	0.11	22	45	185 (d)	49	59	(f)(g)
105	33	3	14.4	0.67	5	59	290 (d)	48	36	(f)(g)
106	13	3	17.4	0.12	4	21	298 (d)	48	35	(f)(g)

(a) initial thiourea concentration = 21 gL^{-1}

(b) per metric ton of precipitate

(c) calculated from solution analysis (3 gm of residue was not sufficient for assay analysis)

(d) determined by assay

(e) stopped stirring overnight - effective leach time may be less than 24 h

(f) initial pH = 0.7; final pH (#103,104) = 1.2; pH (#105) = 0.92; pH (#106) = 0.8

(g) filtrate #104 is very yellow, #105, 106 are slightly yellow in colour

(h) a white precipitate observed in filtrate after 24 h

(i) see methods for description of calculation